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L. M. Dubnikov and I. F. Tikhomirov

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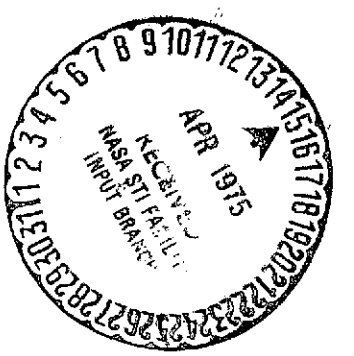

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16. Abstract

A discussion is given on basic studies on determining small amounts of fluorine which were published through 1944. All of the studies have been systematized according to the method of determination and are examined in chronological order.

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THE DETERMINATION OF SMALL AMOUNTS OF FLUORINE*

L. M. Dubnikov and I. F. Tikhomirov

1. Qualitative Methods

The Microcrystalloscopic Method

Small amounts of fluorine can be qualitatively determined according to the formation of the characteristic crystals of sodium or barium fluorosilicates, which was indicated by Huisse [1]. The minimum amount of fluorine detectable by this method — 0.4 - 0.15 μg — was determined by Kley [2]. To establish the presence of fluorine in mineral water, Casares [3] recommends evaporating 150 ml water, to which silver sulfate and powdered glass have been added, in a crucible. During treatment of the dry residue with sulfuric acid, the liberated silicon fluoride reacts with a 1% solution of barium acetate, a drop of which is placed on the lower side of the glass covering of the crucible. /774**

*This survey cites basic studies on determining small amounts of fluorine that were published through 1944 inclusively. Several of those published before 1930 are cited according to a survey published in Mikrochemie, Vol. 27, 1938, p. 265. All of the studies have been systematized according to the method of determination and are examined in chronological order.

**Numbers in the margin indicate pagination in the original foreign text.

Geilmann [4] points out that 1 - 3 µg fluorine can be detected qualitatively proportional to the formation of fluorosilicate crystals. The application of barium compounds alters the detectable minimum to 0.5 - 1 µg fluorine.

Poda [5] considers the minimum detectable amount of fluorine to be 10 µg when judged according to the formation of sodium fluorosilicate.

For determining fluorine in wine, Bolavoine [6] used the phenomenon of turbidity during the reaction of silicon tetrafluoride with water. A content of 1 mg fluorine in 100 ml solution can be detected in this fashion.

Deniges [6a] established that one can detect 1 mg fluorine according to the formation of the characteristic crystals of Hg_2F_2 as the result of reaction of the investigated liquid with 1 drop of solution containing 10 g $Hg_2(NO_3)_2$ in 10 ml HNO_3.

The Method of Glass Etching

Woodman and Tablot [7], as early as 1906, reported the possibility of detecting small amounts of fluorine using the glass etching method. They recommend precipitating the fluorine-ion with barium acetate in the presence of potassium sulfate, since small amounts of fluoride coprecipitate with the barium sulfate during this process. The filtered and dried precipitate is treated with sulfuric acid in a platinum crucible after burning the filter, and the hydrogen fluoride liberated during the process acts on the glass surface. According to the data of the authors, a solution containing 0.1 mg potassium fluoride per liter of water yields a clearly defined reaction. With more careful treatment, one can still detect etching of the glass, even with a 5-fold dilution of this solution.

Olivier [8], in determining small amounts of fluorine in ores, /774
isolated it in the form of silicon tetrafluoride, which was absorbed

by drops of water located on the outer surface of a glass shet covering the reaction vessel. Glass etching was observed over an area limited by the dimensions of the drop during this process. The minimum detectable amount of fluorine is 0.1 μg.

Bruning and Quast [9] also recommend determining fluorine by the glass etching method in toxicological analysis. For this purpose, the ground material is mixed with milk of lime and copper sulfate, the liquid is evaporated until dry, and the residue is carefully calcined. Concentrated sulfuric acid is added to the ash placed in a platinum crucible, and the crucible is covered with a glass sheet. The etched places on the glass are quite visible in the magnifying glass in reflected light. The detectable minimum is 10 μg fluorine.

Essery [10] determined small amounts of fluorine using the glass etching method and employing a lead test tube tightly covered with a glass sheet. For this purpose, the test tube containing the reagent and the substance being measured is placed for two days in a thermostat at 37°. Using this method, one can observe etching with 2 mg fluorine per 100 g substance, if observation is carried out with the aid of a powerful magnifying glass.

Caley [11] indicates that glass etching can detect up to 25 μg fluorine, and that comparison with a standard permits approximate juegment on the quantitative content of fluorine in the analyzed material.

The Method of Altered Glass Wettability

Fetchenheier suggested the use of altered sulfuric acid glass wettability for qualitatively determining fluorine. This reaction, in the author's opinion, makes it possible to detect 0.01% flourine in one minute.

Using this phenomenon, Hagen [12] suggested the following method: A small amount of potassium bichromate crystals are dissolved in 1 ml hot concentrated sulfuric acid in a narrow test tube. The obtained chromium mixture degreases the walls of the test tube until such time as the chromium mixture uniformly flows from the surface of the glass. After this, a few grains or a drop of the investigated solution is added, and the contents of the test tube are heated to the boiling point. If there were fluorine in the investigated material, then upon shaking the test tube, the formation of unwettable spots on the glass would be clearly noted, from which the thin film of chromium mixture separates. With a significant flourine content, this phenomenon ensues instantaneously, even without heating. The detectable minimum of fluorine using this method is 0.5 µg per drop. According to the data of Hagen, the presence of salts of the other halogens, as well as nitrates, phosphates, carbonates, and compounds of sulfur, titanium, uranium, and vanadium, do not interfere with the determination of fluorine. The presence of iron and molybdenum decreases the sensitivity of the reaction. Thus, if the investigated solution is unimolar with respect to $FeSO_4$ or K_2MoO_4, then, according to the Hagen method, one can detect no less than 1 µg flourine. The detection of fluorine by this method is also prevented by ions of boric and silicic acids, which form stable complex compounds with it. However, if the solution is 0.5 mol with respect to H_3BO_3, or contains 0.3% SiO_2, then one can still detect the presence of 5 µg fluorine.

Dubnikov and Tikhomirov [13] found that the most suitable vessel for conducting the reaction was a U-shaped tube with an inner diameter of 4 - 5 mm, and having a capillary neck of 1 mm. For determining fluorine, a small amount of potassium bichromate crystals are dissolved during heating in concentrated sulfuric acid inside the U-shaped tube. The obtained chromium mixture degreases the walls of the tube upon heating to a point at which they are not uniformly wetted. Then a drop of the investigated solution is added to one end of the reaction tube, and 3 to 5 minutes later the appropriate inclination forces the level of liquid in it downward. In the

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presence of fluorides, the chromium mixture remaining on the walls of the film immediately breaks up or slips. The detectable minimum depends upon the composition of the glass of the reaction tube, and fluctuates from 0.2 μg (for quartz) to 0.5 μg fluorine in the drop. Sensitivity increases with the decrease in tube diameter. Thus, in a tube 5 mm in diameter, unwettability is observed with a fluorine content of 0.4 μg per drop, while an increase in diameter to 10 and 15 mm, respectively, increases the detectable minimum to 1 and 10 μg.

The presence of borates and silicates significantly increases the detectable minimum. Thus, with a content of 110 μg boron in the drop, in this volume one can detect no less than 50 μg fluorine, while with the same content of silicon one can detect no less than 20 μg fluorine. The contents of copper, magnesium, zinc, aluminum, titanium, zirconium, vanadium, sulfur, trivalent chromium, molybdenum, wolfram, uranium, iron, heptavalent manganese, as well as carbonates, phosphates, chlorides, bromides, iodides, do not interfere with the detection of fluorine. It has been established that this method is also applicable for detecting fluorine in the organic compounds in which this element is bound with carbon.

The Precipitation Method

The reaction of precipitation of the fluorine-ion by calcium or barium chlorides, usually employed in macroanalysis, has limited significance for microdetermination as the result of a noticeable solubility of the corresponding fluoride salts.

Gautier and Clausmann [14] still consider the use of barium salts most expedient, since the poorly soluble compounds of this element, particularly its fluoride, precipitate with barium sulfate. This method can be used to precipitate fluorine, even with a content of 1 - 0.25 mg/l. The precipitate liberated and isolated from the silicic acid is dissolved with concentrated sulfuric acid in a small crucible, and the presence of fluorine is recognized according to etching. Using this method, one can still detect from 1 to 50 μg fluorine.

Meyer and Schulz [15] precipitate fluorine with lanthanum acetate. This reaction makes it possible to detect 0.01 mg fluorine, and is more sensitive than that based upon the use of thorium acetate. For determining flourine, a 10 ml solution is acidified with acetic acid and is added to a chilled excess 1% solution lanthanum acetate; then dry ammonium acetate is added and the mixture is boiled. After cooling, lanthanum fluoride falls out as a precipitate. With very small amounts of fluorine, the precipitate falls out only after several hours.

Ulex [16] considers the lanthanum method of detecting fluorine in food products the most sensitive one. Thus, for example, egg yolk fluorine forms a significant precipitate. Luhrig [17] also indicates the significant advantage and universal capacity of employing the method of fluorine precipitation in food products analysis with the aid of lanthanum acetate, as the result of its high sensitivity, rapidity, and simplicity. Cadenbach [18] detects fluorine in organic compounds by preliminary drying of the substance in a hydrogen stream. The gaseous products of combustion pass through a solution of lanthanum acetate, and the presence of fluorine is recognized by the liberation of the precipitate. This method can also be used for macroquantitative determination of fluorine.

According to Fischer [19], fluorine is detected in 1 ml fluoride acetate solution by adding 0.5 ml saturated solution sodium acetate to a drop of 0.2% solution eosin and 0.5 ml 1% solution lanthanum acetate. After prolonged boiling, the solution is cooled and centrifuged. In the presence of fluorine, a precipitate of lanthanum fluoride falls out that is stained red. For microdetermination, three drops of the investigated solution are mixed with one drop of acetic acid solution of sodium acetate (acetic acid saturated with sodium acetate 1 : 1, with 1 drop 0.1% solution eosin and 3 drops 1% solution lanthanum acetate). After a short period of boiling, the material is cooled and centrifuged. The precipitate falls out in the presence of as little as 2 μg fluorine. Determination is not disturbed by the ions SO_4'', Cr_2O_7'', SiO_3', Cl', NO_3', NO_2', ClO_3',

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ClO_4'; the ions PO_4''', MoO_4'', CrO''_4, and SO_3'' interfere with determination.

I. V. Tananayev [20] determined fluorine in the form of calcium fluoride. The impurities interfering with determination were preliminarily removed with silver nitrate. For this purpose, 5 ml investigated solution was alkalated with caustic soda to a clear rose color according to phenolphthalein, and having added the excess $AgNO_3$, heated. The precipitate is separated by filtration, and a solution of $Ca(NO_3)_2$ is added to the filtrate. The appearance of turbidity or a precipitate indicates the presence of fluorine. The detectable minimum is 0.2 mg per 5 ml.

Pertusi [21] suggested using the reaction of yellow precipitate formation to detect fluorine; the yellow precipitate forms in reaction to cold under the action of benzidine acetate, even in reaction to a very dilute solution of fluorine, and in the presence of mercuric acetate. The precipitate, having a composition of HgF_2 $(HFNH_2C_6H_4C_6H_4NH_2HF)_2$ is insoluble in water, alcohol, ether, and the other organic liquids, but dissolves easily in acids, and is broken down by the alkalis.

The Colorimetric Method

Smit [22] employed the method of Greef [23] for a qualitative determination of traces of fluorine; Greef suggested the method for a quantitative determination. The method is based upon discoloration of ferrous thiocyanate by the fluorine ion due to the formation of the complex ion FeF_6^{-3}. The reaction is conducted in the following fashion: The test solution is mixed in a reaction vessel having a capacity of 10 ml with 0.5 ml 10% solution potassium thiocyanate and a 0.1% alcohol solution of iron chloride is added until the mixture attains an orange color; the ferrous chloride is added drop by drop (from a micropipette). Simultaneously, aqueous solutions are

prepared that contain the same amount of $FeCl_3$ and KSCN. Potassium fluoride is added from the micropipette until the same orange color of the liquid is obtained. By using this method, one can detect 0.05 mg fluorine in 10 ml solution.

Dubnikov and Tsvik [24] detected small amounts of fluorine by using this method in the modification of Greef and Chemodanova [25], and in order to increase the accuracy of determination, the examined layer of liquid was increased. Tubes made of brown glass were used as the cuvette; the tubes had an internal diameter of 1.5 mm, and a length of 240 mm; one of them was used for the test solution, while the other was used for the standard solutions.

0.4 ml indicator (1.5 ml 2.4% solution ammonium thiocyanate plus 0.2 ml 5% solution potassium persulfate plus 0.25 ml alcohol solution of ferrous chloride containing 1 mg iron per 1 ml) are added to 5 ml investigated liquid and 5 ml distilled water. To each cuvette are added 5 ml liquids prepared in this fashion, and their colors are compared. A change in color under these conditions is observed only with a fluorine concentration of 1 mg/l. If 0.2 ml indicator, rather than 0.4 ml, is used per 5 ml liquid, one can quite adequately clearly observe yellowing with a fluorine ion concentration of 0.4 mg/l. A further decrease in the amount of the indicator does not increase the sensitivity of determination.

This reaction can still detect 1.2 μg fluorine in 5 ml solution if the fluorine is in the form of the fluoride, and in the amount of 3 μg if it is in the form of silicon fluoride. /777

Gol'denberg [26] used the method of Steiger [27], based on discoloration of a solution of titanium sulfate with hydrogen fluoride in the air.

$$H_2[TiO_2(SO_4)_2] + 6HF = H_2TiF_6 + 2H_2SO_4 + H_2O_2.$$

In order to detect fluorine, 2 ml solution titanium sulfate is added to the investigated liquid (1 ml solution titanium sulfate contains 0.1 mg TiO_2), 2 - 3 ml H_2O_2, and the solution is diluted with water in an amount up to 25 ml, and compared with the color of the standard solution. The salts of aluminum and iron, as well as the silicates and phosphates, interfere with the determination and must be preliminarily removed by treatment with ammonium carbonate and precipitation with silver nitrate. This method can detect from 0.1 to 1 mg fluorine in 25 ml solution.

L. Kul'berg [28] suggested the following method of detecting fluorine: If one places a drop of ferrous thiocyanate solution on filter paper and the thiocyanate solution contains a large excess of ammonium thiocyanate, and one adds a drop of yellow potassium ferrocyanide to the formed spot, the spot will become an emerald green, and after a short period of heating — gray. In the presence of fluorine, a blue-violet color appears. The reaction makes it possible to detect 0.033 μg fluorine ions per microdrop with a maximum dilution of 1 : 50,000. Borates, silicates, chromates, and ferricyanides interfere with determination. In the absence of these substances, one proceeds in the following fashion. To 0.2 ml investigated liquid one adds from 3 to 10 drops of 0.1 N. nitric acid in a small crucible; the mixture is slowly heated to break down the nitrides, sulfides, carbonates, and cyanides, if they are present in the analyzed solution. Then the liquid is neutralized in the presence of a drop of methyl red with a 0.1 N. solution KOH, and by adding a drop of 0.04 N. HNO_3, brought to a clearly rose color. A drop of solution containing 2 ml water with 0.025 g ferrous ammonium alum and 1 g ammonium thiocyanate is placed on a thin, dense piece of filter paper. A drop of saturated solution of potassium ferrocyanide is applied to the obtained spot. The spot is lightly dried, and a drop of the investigated solution is applied. In the presence of the fluorine ion, blueing is observed. In order to detect fluorine in an unknown mixture of anions, 3 - 4 crystals of sodium acetate are added to 0.2 - 0.3 ml neutral solution in a watch glass, and upon heating, a solution of $AgNO_3$ is added drop by drop. The excess $AgNO_3$ is then

precipitated by 1 - 2 drops of concentrated solution NaCl. Fluorine is detected as described above in the filtrate from the formed precipitate.

De-Boer [29] discovered that zirconium alizarin sulfate stains a raspberry color in the presence of the fluorine ion.

$$[C_{14}H_6O_4SO_3H]_4\,Zr + 6NaF + 4HCl \rightarrow Na_2ZrF_6 + 4C_{14}H_7O_4SO_3H + 4NaCl.$$

The liberated alizarin sulfate stains yellow, as a result of which the color of the solution can change from raspberry to yellow, depending on the fluorine content. The reactive prepared by mixing 2 ml 1% - solution $ZrOCl_2 \cdot 8H_2O$, 5 ml 0.3% solution alizarin sulfate, and 60 ml concentrated hydrochloric acid changes from raspberry to yellow in the presence of as little as 1 µg fluorine per 1 ml. In a case of increasing the amounts of hydrochloric acid twfold, a tenfold increase in reaction sensitivity occurs.

Pavelka [30] developed the drop method of determining fluorine with the aid of zircon-alizarin reactive paper. For its preparation, he employed free alizarin, instead of alizarin sulfate of sodium. The drop reaction was carried out with pure fluoride in the presence /778 of a 50% solution of acetic acid. With a content of 10 µg fluorine, the yellow stain ensues instantaneously, but in the case of small amounts the reaction can be accelerated by heating. Impurities of sulfates, oxalates, and phosphates that interfere with the determination of fluorine can be eliminated, or the fluorine can be extracted from such mixtures in the form of SiF_4. Fluorine in SiF_4 can also be determined by employing moistened zirconium-alizarin paper.

In order to determine small amounts of fluorine in silicate rocks, Alimarin [31] also used the zirconium-alizarin method. The indicator was prepared by mixing 3 volumes of solution of 1 g $Zr(NO_3)_4$ in 250 ml water with 2 volumes of solution of 1 g alizarin red in 250 ml ethyl alcohol. An area of filter paper is soaked with this indicator and dried in air. For determining fluorine, a drop

of diluted hydrochloric acid (1 : 20) is applied to the indicator paper, followed by a drop of the investigated solution. With a content of 50 μg fluorine per 1 ml, a yellow spot appears in a few minutes. The detectable minimum can be decreased to 2 μg fluorine per 1 ml if the indicator is diluted with 50 times the amount of water. The fluorine is driven from the minerals in the form of boron fluoride, and following solution in water is determined according to this method.

Stone [32] indicates the advantages of employing free alizerin and recommends preparing an indicator by dissolving 0.5 g alizarin upon heating in 200 ml alcohol, and 1.5 g $ZrCl_4$ in 75 ml alcohol. Both solutions are mixed and heated, and the zirconium-alizarin "lac" falls out; it is filtered and washed with alcohol. The moist precipitate is mixed with alcohol to a volume of 25 ml, and 5 ml of this suspension is mixed with 100 ml concentrated hydrochloric acid. According to Stone's data, 0.3 mg flourine contained in the solution causes an instantaneous change in color; in the presence of 0.15 mg fluorine, this phenomenon ensues after 5 seconds, while with 0.03 mg — after 15 seconds. If sulfates, phosphates, and oxalates are absent, one can detect even 1.5 μg fluorine in 5 ml liquid with 0.1 ml indicator over a period of 5 minutes. The reaction is also applicable for detecting fluorine in the complex fluorides. During the use of reactive paper impregnated with the zircon-alizarin lac, 0.3 mg fluorine per 1 ml can be detected.

Koone [33] prepared a zircon-alizarin lac by mixing alcohol solutions of alizarin (0.5 g in 200 ml) and zirconium chloride (1.5 g and 75 ml). The formed precipitate is filtered, mixed with 25 ml alcohol, and diluted with water up to 100 ml. A change in color from red to yellow is caused by 0.03 - 0.3 fluorine in a period of 5 seconds. The reaction should not last longer, since sulfates, oxalates, and phosphates can unfavorably affect the color. The free halogens that interfere with detection reduce the sodium sulfite before oxidation.

Baroni [34] used a zirconium-alizarin solution to detect fluorine in flask glass, since the presence of this element causes turbidity or even the fallout of precipitates in solutions intended for injection.

In order to detect hydrogen fluoride in the air of a superphosphate plant, Korenman [35] also used zirconium-alizarin paper. The detectable minimum is 2 μg HF per liter of air.

Feigl and Reimann [36] suggested a method of determining fluorine by the aid of reactive paper impregnated with zirconium azarsinate. If the acidified drop of the tested solution is placed on reactive paper, the presence of F' is recognized according to the formation of a red paradimethylaminoazophenyl arsinic acid liberated in the free form. This method is 80 times more sensitive than the /779
zirconium-alizarin method. The detectable minimum is 0.25 μg fluorine; the maximum concentration is 1 : 200,000. In the presence of interfering impurities, fluorine can be extracted in the form of SiF_4.

Kolthoff and Stansby [37] determined fluorine with the aid of a zirconium-purpurin indicator. For preparing the indicator, 0.16 g zirconium oxychloride $ZrOCl_2 \cdot 8H_2O$ is dissolved in 100 ml concentrated hydrochloric acid, and is diluted with 100 ml distilled water. Simultaneously, 9 mg purpurin is dissolved in 30 ml ethyl alcohol, and both solutions are mixed. To the obtained mixture, one adds 620 ml concentrated hydrochloric acid and dilutes it with up to a liter of water. The next day, the indicator is suitable for use; it remains stable for a month. To detect fluorine, a substance is dissolved in 2 ml 6 N. hydrochloric acid, and 2 ml indicator are added. With a fluorine content of 3 μg or more, the rose color immediately changes to yellow.

Feigl, Krumholz [38, 39] determined fluorine according to the blue color that appears during the reaction of benzidine with silicic-molybdenum acid.) With this goal, the fluorine is extracted in the form of SiF_4, and the latter reacts with a drop of water located on the inner surface of a glass sheet covering the reaction

vessel. The formed silicic and silico hydrofluoric acids change into silico molybdenum acid under the action of ammonium molybdate; the silicomolybdenum acid oxidizes the benzidine in the acetic acid solution to a bluer pigment that simultaneously reduces to molybdenum blue. The detectable minimum is 1 μg fluorine.

The Spectroscopic Method

Papish, Hoogund, and Snee [40] conducted spectroscopic determination of fluorine by decomposing a mixture of fluor-containing substances with calcium salt in a voltaic arc. The visible line at $\lambda = 5291$ Å corresponds to the fluor-calcium band, and is constant. It can be induced by 10 μg fluorine; however, practically such amounts as 20 μg are difficult to recognize.

Ahrens [41] spectroscopically determined the fluorine in the phosphorites. With a normal arc discharge in the spectrum, the lines or bands corresponding to fluorine are not found, but they do appear if the fluorine is bound with Be, Mg, Ca, Sr, or Ba.

Paul [42] determined fluorine spectrographically in the form of silicohydrofluoric acid slats. The detectable minimum is 110 - 120 μg fluorine.

In conclusion of the survey of the qualitative methods of determining fluorine, Table 1 is provided. Table 1 indicates the detectable minimum, interfering impurities, and the direction of analysis.

TABLE 1. QUALITATIVE DETERMINATION OF FLUORINE

Author	Ref.	Detectable minimum	Determination time	Amt. of sample or sol'n	Ions interfering with detection
		Microcrystalloscopic method			
Kley	2	0.4-0.15 μg			
Geilman	4	0.5-3 μg			
Poda	5	10 μg			
Bolavoine	6	1 mg in 100 ml			
		Glass etching			
Woodman	7	1 part KF in 10 million			
Olivier	8	0.1 μg per drop			
Bruning	9	10 μg			
Essery	10	2 mg in 100 g	48 hrs		
		Change in glass wettability			
Fetkengeyyer	43	0.01%	1 min		
Hagen	12	0.5 μg	1 min	Drop	BO_2^-, SiO_3^{-2}
Dunikov	13	0.2-0.4 μg	1 - 5 min	"	BO_2^-, SiO_3^{-2}
		Precipitation method			
Gautier	14	1 - 50 μg			
Meyer	15	10 μg	Several hrs	10 ml sol'n	
Tananayev	20	0.2 mg		5 ml	
Fischer	19	2 μg	Several hrs	3 drops	PO_4^{-3}, MoO_4^{-2}, CrO_4^{-2}, SO_4^{-2}
		Colorimetric method			
Smit	22	0.05 mg		10 ml	Al^{+3}, SiO_3^{-2}, Fe^{+3}
Dubnikov	24	1.2 μg	5 min	5 ml	PO_4^{-3}
Gol'denberg	26	0.1-1 mg		25 ml	BO_2^-, SiO_3^{-2}, CrO_4^{-2}, $Cr_2O_7^{-2}$, $Fe(CN)_6^{-3}$
Kul'berg	28	0.033 μg		0.002 ml	SO_4^{-2}, $S_2O_8^{-2}$, PO_4^{-3}, AsO_4^{-3}, CrO_4^{-2}
De-Boer	29	1 μg		1 ml	
Pavelka	30	10 μg		Drop	
Alimarin	31	2 - 50 μg	Several min	1 ml	

(Table continued on following page)

TABLE 1. (continued)

Author	Ref.	Detectable minimum	Determination time	Amt. of sample or sol'n	Ions interfering with detection
Stoone	32	1.5 μg	5 min	5 ml	SO_4^{-2}, PO_4^{-3}, CrO_4^{-2}
		30 "	15 sec	100 ml	SO_4^{-2}, PO_4^{-3}, CrO_4^{-2}
		150 "	5 sec	100 ml	SO_4^{-2}, PO_4^{-3}, CrO_4^{-2}
		300 "	Instantaneous	100 ml	SO_4^{-2}, PO_4^{-3}, CrO_4^{-2}
Koone	33	30 - 300 μg	5 sec	100 ml	
Korenman	35	2 μg HF	Instantaneous	1 l air	
Feigl	36	0.25 μg	"	1 drop	
Kolthoff	37	3 μg		4 ml	NO_3^-, NO_2^-, BO_2^-, CrO_4^{-2}, $C_2O_4^{-2}$, PO_4^{-3}, Cl^-, Br^-, SO_4^{-2}, SO_3^{-2}, S^{-2}
Feigl	38,39	1 μg		1 - 2 drops	CO_3^{-2}, S^{-2}, J^-, Br^-, Cl^-

II. Quantitative Determination of Fluorine

The Colorimetric Methods

a) Methods based on the formation of complex titanium compounds. /781

Steiger [27] first determined small amounts of fluorine colorimetrically by staining the yellow complex $H_2[TiO_2(SO_4)_2]$. For analyzing 20 ml solution titanium sulfate in 1 ml 0.1 mg TiO_3 and 30 mg H_2SO_4, 3 ml hydrogen peroxide and 74.5 ml water are mixed with 1.5 ml test solution. The amount of fluorine is determined according to the degree of staining. The detectable minimum is 0.75 mg fluorine in 1.5 ml sample. A proportionality between the intensity of stain and the fluorine content is not observed; therefore, a calculation curve is constructed which is used for the determination of fluorine. The presence of iron, aluminum, phosphoric and silicic acid distort the results of the analysis, as a result of which these substances must be removed by means of preliminary treatment of the sample.

Mervin [44] established that a high concentration of sulfates of the alkali metals weakens the intensity of staining of the titanium complex, while the free acids enhance it. For determining fluorine in minerals, the author developed a special course of analysis and formulas for calculations making it possible to take into account the effect of free acids and the salts of the alkali metals. By using this method, one can determine from 0.5 to 4.0 mg fluorine. According to the data of Adolf [45], the Steiger-Mervin colorimetric method is quite suitable for detecting and determining fluorine in minerals. Fresenius [46], having verified and improved this method, indicated that it yields good results with a test content of 3 - 4 mg fluorine. With a content of 0.5 - 0.05 mg, the results were unsatisfactory. Gol'denberg [26] altered the method of Steiger, having employed titration of a standard solution of titanium with a solution of sodium fluoride to obtain identical readings of the colorimeter. For preparing the standard solution of titanium not containing fluorine, a suspension of titanium sulfate is dissolved in water and a large excess amount of sulfuric acid is added; the mixture is heated to the point of appearance of sulfurous anhydride vapor, then water is added and the mixture is once again heated. After this treatment, water is added to a content of 0.1 mg TiO_2 per 1 ml, and the concentration of sulfuric acid in the prepared solution must be 3%. Determination of fluorine with a content lower than 0.1 mg per 100 ml solution does not yield accurate results.

Korenman [35] uses solutions of $Ti(SO_4)_2$ containing 0.75 mg titanium dioxide in 25 ml solution for determining small amounts of fluorine. For analysis, 5 ml solution titanium sulfate and 3 ml 3% hydrogen peroxide are added to the investigated liquid, after which the mixture is brought to 25 ml by adding water. Standard solutions containing measured amounts of fluorine are prepared in the same fashion. The error of this method does not exceed 0.01 mg HF per 25 ml solution.

Wichmann [47] employed a photocolorimeter, and developed the best conditions for determining small amounts of fluorine by the

Steiger-Mervin method. The author directed his attention to the necessity of observing a strictly determined pH of the solution. With a pH of 1.5, the intensity of staining reaches the highest value, after which it falls, and at pH = 2.5, falls to 0.

The detectable minimum depends on the concentration of titanium and fluoride, and diminishes in the presence of aluminum, sulfates, and phosphates.

Shvedov [48], having used the photocolorimeter, checked the Steiger method for solutions containing from 0.55 to 5 mg fluorine per liter, finding the average accuracy of determination to be 0.1 - 0.2 mg/liter.

b) Methods based on the formation of complex iron compounds. The first method of quantitatively determining dissolved fluorides of iron salts was suggested by Guyot [49] in 1870. In the Greef modi- /782
fication [23], 20 g sodium chloride and 5 ml 20% solution ammonium thiocyanate are added to 25 ml of the investigated solution, after which the liquid is titrated to the appearance of a light yellow stain of the ferric chloride solution, 100 ml of which corresponds to 1g NaF. Then 10 ml ether is added and titration is continued to the point of a red stain of the ether layer. The method is based on the formation of a colorless complex ion FeF_6^{-3}. The appearance of the red stain indicates the termination of titration. According to the data of Treadwell [50] and Korenman [35], this method is only suitable for determining large amounts of fluorine on the order of 200 g. Smit [22] found that the determination of fluorine using this method is best conducted with an alcohol solution of ferric chloride, and according to the author's data, one can determine from 0.05 to 0.5 mg fluorine per 10 ml.

Foster [51, 52] altered the Greef method for determining fluorine in water in the following fashion: To a solution of ferric chloride taken in excessive amount, one adds a known amount of fluoride and carries out colorimetry in the presence of thiocyanate.

According to these data, a calculation curve is constructed which is then used for determining the content of fluorine in the investigated sample. This method can be used to detect from 0.025* to 0.25 mg fluorine in the 75 ml solution.

The results of measurement are affected by the presence of sulfates, chlorides, nitrates, borates, and phosphates. Thus, 200 mg sulfate in a liter is equivalent to 0.5 mg chlorine; 500 mg chloride in a liter is equivalent to 0.1 mg fluorine.

Sanchis [53, 54] considers the Foster method the best of all methods of determining fluorine that are based on the formation of complex ferric fluoride. The shortcomings of the method include occasionally poor duplicability of results, since staining quite rapidly diminishes and strongly depends upon medium pH.

Schvedov [48] photocolorimetrically verified the Foster method for a fluorine content ranging from 0.5 to 3 gm/ℓ, and established the absence of a linear relationship between the content of fluorine and the change of color. Deviations between the parallel measurements reach 0.3 mg/ℓ.

In employing this method, Chemodanova [25] developed a good method of determining hydrogen fluoride in the amount of 0.001 - 0.015 mg/ℓ in air.

Shakhkel'din and Serdobova [55] consider the accuracy of determining fluoride according to the ferrous thiocyanate stain to be 1.3% with a fluorine conent to 30 mg/ℓ. M. Fel'dman [56] also recommends this method for determining the amount of fluorine in the air of plants used for electrolytic aluminum extraction. The detectable minimum during work with the photocolorimeter with the selenium photoelement is 0.002 - 0.032 mg fluorine per liter of air. The ferrous thiocyanate stain does not change at a temperature range

*Translator's note. Erroneously given in original foreign text as 0.25. Range from 0.025 to 0.25 is confirmed in Table 2.

from 10 to 22°, accelerates | below 10°, and above 22° the stain weakens.

Armstrong [57] suggested a method of determining fluorine based on the staining of iron complexes with acetyl-acetone. The presence of 50 mg sodium chloride or 100 mg sodium sulfate, 400 mg sodium sulfite or the same amount of sodium nitrate, as well as small amounts of silicic acid in 25 ml investigated liquid do not interfere with determination. Wilcox [58] determined fluorine photocolorimetrically according to the method of Armstrong, and found that the acetyl-acetone reagent is somewhat less sensitive to the effect of sulfates than the thiocyanate one. The accuracy of the method is 0.1 mg/l fluorine.

c) Methods based on a change in the color of zirconium-alizarin, zirconium-purpurin, thorium-alizarin, and other lacs. De-Boer [29] used a staining reaction of the zirconium-alizarin complex for determining fluorine, and subsquently [59] suggested a new quantitative method for determining fluorine solutions, complexes, insoluble fluorides based on this reaction. Two identical volumes of a hydrochloric acid solution of zirconium oxychloride are used for analysis according to this method; to one of these one adds the investigated solution, and after adding sodium alizarinoxysulfate, both solutions are titrated with potassium fluoride in a known concentration to an identical color. The content of fluorine in the investigated liquid is determined according to the difference in the amount of fluoride entering the titrations. This method also yields good results when determining fluorine in K_2BeF_4, KBF_4, Na_2SiF_6, CaF_2, MgF_2, PbF_2, and Na_3AlF_6. All these flourides are preliminarily dissolved in an acid solution of zirconium oxychloride, and fluorine is determined by colorimetric titration. The presence of sulfates, thiosulfates, phosphates, arsenates, and oxalates prevents obtaining accurate results. Subsequent attempts were made to improve this method by either removing fluorine from the impurities by distillation or by altering the method of preparing the indicator and the technique of colorimetric titration.

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Thompson and Taylor [60] studied the effect of different salts of sea water on the accuracy of analysis. When analyzing a sample containing fluorine in the amount of 0.8 - 1.6 mg/l and impurities of various salts, hydrochloric acid and an indicator were added. Then the mixture was rapidly heated to the boiling point, cooled, and after 4 hours its color was compared in Nessler pipettes with the color of standard solution. It was established that bromides, iodides, carbonates, nitrates, phosphates, and silicates, as well as the salts of calcium, barium, potassium, and strontium, in the amounts encountered in sea water do not affect the change in indicator color. Ions of iron oxide and ferrous oxide also do not practically affect determination with a content of up to 10 ml/l. The error of analysis did not exceed 0.05 mg fluorine in samples of water containing fluorine in amounts ranging from 1 to 2 mg/l.

Elvove [61] increased the concentration of acid when determining the amount of fluorine in drinking water using the method of Thompson and Taylor, and found that the best results are obtained with a content ranging from 0.8 to 1 mg fluorine per liter. Under these conditions, the error of analysis did not exceed 1.5%.

Barr and Thorogood [62] found that the accuracy of determining fluorine in water using this method is 0.1 mg/l fluorine with a content up to 5 mg/l. Entirely clear results are obtained only with a fluorine content no higher than 2 mg/l.

Sanchis [53, 54] studied the effect of impurities on the detectable minimum of fluorine. A mixture of solutions of sodium alizarinoxysulfate and zirconium nitrate served as the indicator. Flourine in amounts ranging from 0 to 3 mg/l prepared in distilled water served as the standard solutions.

Measurement is unaffected by chlorides, sulfates, bicarbonates, and the salts of sodium, calcium, and magnesium in amounts up to 500 mg/l, manganese salt in the amount up to 200 mg/l, silicate salts up to 50 mg/l, phosphate salts, boron compounds, iron compounds,

and copper compounds up to 5 mg/l, and up to 2 mg/l sulfides. The level of error is ± 0.1 mg fluorine per 1 liter.

A subsequent study indicates that the presence of up to 0.5 mg/l aluminum does not diminish the accuracy of measurement. The intensity and shades of color of the solution depend upon both the concentration of the indicator and the concentration of acid. The following solution are employed: sodium fluoride — 1 ml contains 0.01 mg fluorine; indicator — 0.17 g sodium alizarin sulfate per 100 ml water, 0.87 g zirconium nitrate per 100 ml water. Zirconium nitrate is added drop by drop during agitation to a solution of alizarin sodium sulfate salt and is left overnight; 20 ml solution is then diluted to 100 ml.

In the Biogeochemical Laboratory of the Academy of Sciences of the USSR [63], methods of determining fluorine in drinking water according to the change of color caused by zirconium, thorium, serium, and other salts with aqueous solutions of purpurin, oxianthraquinone and alizarin were checked. The best proved to be an indicator suggested by Sanchis. The method of analysis [64] consists /784 in the following: 1 liter of the investigated water is alkalized and boiled dry. The residue is calcined, and 100 ml sulfuric (or perchloric) acid and water are added to obtain a mixture that boils at 110°. HF is distilled at 135 degrees. After distilling 30 - 50 ml, heating is terminated and the mixutre is diluted with water to the initial state, after which 30 - 50 ml are distilled again into another receiving flask. The same operation is repeated 3 times. Fluorine is determined colorimetrically according to the Sanchis method in each of the 3 fractions. According to the authors' data, the accuracy of measurement can be brought to ± 0.01 mg fluorine per liter. The method is only suitable under conditions of a fluorine content ranging from 0.1 to 2.5 mg/l in the investigated sample.

At the Scientific Research Institute Laboratory of Communal Hygiene of the Leningrad City Department of Public Health [65], a colorimetric method of determining fluorine in water was suggested

and developed. For conducting the analysis, 500 ml investigated water is alkalized with 2 - 3 drops 1 N solution alkali, and is boiled down in a round-bottom flask to 100 ml. To the obtained residue, several grains of quartz and 20 ml sulfuric acid (1.84) are added. After this, the contents of the flask are distilled at a temperature of 130 - 140°, maintaining the volume by periodically adding distilled water to the flask through a drip cock. The distillate, collected in an amount no less than 150 ml, is alkalized with 2 drops of alkali, and is evaporated down to about 90 ml. The solution is poured into a measuring cylinder to which 2 ml 3 N hydrochloric acid, 2 ml 3 N sulfuric acid, 2 ml zirconium-alizarin indicator, and up to 100 ml water are added.

The mixture is heated in an Ehrlenmeyer flask to the boiling point and left for a day. Simultaneously, standard solutions are prepared in the same fashion, using double distilled water. The accuracy of the method is such that up to $\pm$ 0.01 - 0.02 mg fluorine per liter can be measured. The authors checked the detectable minimum under different experimental conditions, and the accuracy of methods of quantitatively determining fluorine in water suggested by Sanchis, Foster, Willard and Vinter, Boruff and Abbot. As a result of the experiments they conducted, it was established that the method suggested by the authors is the simplest and most accurate, particularly with a content of hundredths of a milligram of fluorine per liter.

Harris and Christiansen [66] measured small amounts of fluorine in phosphates using the Sanchis method, carrying out distillation with a 60% perchloric acid solution at 135 - 150°. Using this method, one can measure up to 0.003% fluorine. Shvedov [48] checked the De-Boer method photocolorimetrically. He prepared samples containing up to 2.0 mg fluorine per liter. A change in color occurred 18 hours after mixing the solutions. The error of the analysis was within limits of from 1 to 5%.

M. Raynes and A. Krupkin [67] studied the photocolorimetric measurement of small amounts of fluorine in salts of aluminum by employing titanium and zirconium-alizarin reagents. They established

that the change in color of the titanium solutions is very slight, and relative error reaches 10%. The use of the zirconium-alizarin indicator yields good results with a change in its amount depending upon the fluorine content. With a fluorine content ranging from 0.01 to 0.1 mg per 100 ml, it is necessary to use 2 ml indicator (prepared according to the Sanchis prescription); with a content ranging from 0.1 to 1 mg fluorine, 5 ml are added; with a content from 0.5 to 2 mg fluorine, 10 ml indicator are added. It was also established that the use of zirconium oxychloride as an indicator yields a less stable stain than the use of zirconium nitrate. The authors also checked measures of distilling fluorine suggested by Tananayev and Armstrong. The best results are obtained according to the method of Tananayev [68], but they are still very low. The most accurate results were obtained by replacing SiO_2, employed for the formation of SiF_4, with ferrosilicon. /785

Raynes and Kazachkova [69] used the photocolorimetric method of determining fluorine by employing zirconium-alizarin, and found that with this method one can determine 0.001 - 0.002 mg per 25 ml solution.

Lamar [70] indicates that methods of determining fluorine summarized in 1941 by the American Water Association [119] proved inadequately accurate for analyzing natural waters containing less than 0.4 mg fluorine per liter. The author recommends a somewhat altered zirconium-alizarin method, suitable for determining fluorine in amounts not exceeding 0.12 mg per 100 ml samples. Particular attention was paid to the accuracy of regulating the pH of the solution.

Talvitie [71] altered the Lamar method, having used thorium instead of zirconium, which accelerates the reaction and increases the stability of the lac. The equilibrium between the reacting components ensues 30 minutes after adding the reagents to the sample. According to the method suggested by the author, one can determine 1 mg fluorine per liter in the presence of up to 100 mg sulfates,

nitrates, and chlorides of calcium and magnesium. The author established that iron, phosphates, and aluminum interfere with the determination of fluorine. When working with this method, 5 ml alizarin indicator are added to 100 ml liquid in an Ehrlenmeyer flask, then 0.3 N nitric acid is carefully added until the appearance of a yellow color. After this, the liquid is transferred to a Nessler tube, and up to 110 ml water are added; 5 ml thorium reagent are added, and the mixture is stirred well. Thirty minutes later, it is compared with the color of the standard solution. The following reagents are used: a 0.001 mol solution of thorium nitrate; a 0.00025 mol solution of sodium alizarin sulfate; a solution of sodium fluoride containing 2.1 mg/l, and a 0.3 N solution of nitric acid.

In 1934, Smit [95] suggested a method of determining fluorine in water with the aid of zirconium-quinalizarin that had been recommended by Willard, i.e., a zirconium substitute of 1,3,5,8-tetrahydroxianthraquinone, which is more sensitive to fluorine. For preparing the indicator, equal parts of a 0.14% solution of quinalizarin in a 0.3% alkali and 0.87% solution of zirconium nitrate are mixed. The mixture is diluted with distilled water in the ratio of 1 : 40. To 50 ml water preliminarily purified of sulfates by adding 5 ml 2% solution $BaCl_2$, 3 ml hydrochloric acid, and 5 ml zirconium-quinalizarin indicator are added and carefully stirred. After 20 minutes, the colorimeter is used to compare the sample color with the color of standard solutions prepared and processed using the same method. Sulfates in the water interfere with measurement if their concentration exceeds 20 mg/l, as do iron ions with a content in excess of 10 mg/l, phosphates in an amount exceeding 0.3 mg/l, and aluminum in an amount exceeding 0.2 mg/l. In the presence of 0.2 - 0.6 mg aluminum per liter, the amount of detectable fluorine decreases to 0.1 mg/l. In the case of the presence of a large amount of impurities interfering with the determination of fluorine, the latter can be extracted using perchloric acid after the method of Boruff and Abbot. The best results are obtained with a content of up to 0.1 mg fluorine per 50 ml.

Kolthoff and Stansby [37] suggested a zirconium-purpurin method of measuring fluorine. To 2 ml investigated solution containing 0.5 - 15 mg fluorine, or to a suspension of solid fluoride mixed with 2 ml water in a 100 ml glass container, 5 ml 10 N hydrochloric acid and 2 ml alcohol 20% solution purpurin (1,2,4,-trihydroxianthraquinone) are added. In another flask, 40 ml standard cobalt-bichromate solution is placed containing 19.6 g $Co(NO_3)_2 \cdot 6H_2O$ and 0.132 potassium bichromate per 1 liter water. Then, to the investigated liquid a solution of zirconium oxychloride containing 0.8 g salt in 1 l 10 N /786
sulfuric acid is slowly added from a burette while constantly stirring the solution; this is continued until the color of the liquid is the same as that of the standard solution. Bringing the total volume of liquid to about 40 ml by adding 10 N hydrochloric acid, titration is continued to the point of complete correspondence of the color with the standard. The amount of zirconium solution expended per 1 mg fluorine should be established beforehand. The error of measurement is 3 - 4%. The standard cobalt-bichromate solution has a yellowish-orange color of the same intensity as a solution containing 0.5 mg zirconium, 38 ml 10 N hydrochloric acid, and 2 ml purpurin solution. It should be borne in mind that with any other amount of zirconium, the color of the solution changes from yellow to violet. The color does not practically depend upon temperature if the standard cobalt-bichromate solution is used, but with the use of the purpurin solution as a standard, a change in temperature has a sharp impact on color.

R. Ye. Osherovich [72] measured fluorine in apatites and phosphorites using the photocolorimetric method. The method suggested by her is based on discoloration of the aluminum-aluminous lac, stained an intensive red. In order to determine the fluorine content, 1 g apatite or phosphorite is mixed with sulfuric acid, and the fluorine is distilled in a container holding 1.5 g potassium chloride; the volume of the distillate is diluted in a measuring flask up to 500 ml. To 10 - 20 ml solution containing 0.06 - 0.14 mg fluorine, 0.04 mg aluminum is added in the form of $AlCl_3$, and 5 ml 1 N hydrochloric acid, 5 ml 3 N ammonium acetate, 5 ml 0.1% solution

aluminonium, and, finally, 5 ml 5 N solution ammonium carbonate are added. The volume of the liquid is increased to 100 ml. Since the intensity of color increases with the passage of time, colorimetry is carried out after 1 hour. The accuracy of measurement is 5 - 6%.

Shvedov [73] improved the method of colorimetric determination of fluorine, having checked the use of alizarin sodium sulfate purpurin, anthropurpurin, flavopurpurin, anthrohallol, alizarin cyanin and cerulein for this purpose. The most sensitive indicator for determining traces of fluorine is 1,2,4,5,8-alizarin cyanin, which can easily be used for determining fluorine in natural water. The effect of K^{+}, Na^{+}, CA^{+2}, Mg^{+2}, Cl^{-}, NO_3^{-} is very slight, while at the same time AL^{+3}, SO_4^{-2}, PO_4^{-3}, AsO_3^{-3}, AsO_4^{-3} interfere, altering the color noticeably.

Faney [74] suggested a colorimetric method of analyzing fluorides in ores, minerals, and natural waters with the aid of ferron (7-iodo-8-hydroxiquinolin-5-sulfo acid). This reagent was earlier used for colorimetric determination of trivalent iron. A mixture of water-saturated solution of ferron with solutions of ferric chloride in hydrochloric acid stains green. In the presence of fluorides, a yellow stain appears. The standard solution, which contains the same reagents as the investigated one, besides fluoride, is titrated with a 0.02 N solution of sodium fluoride until a correspondence of color occurs. The use of the colorimeter makes it possible to detect 2 mg fluorine per liter of solution using this method.

Volumetric Methods

Direct volumetric determination of fluorine is possible only in certain cases, and one is usually forced to extract fluorine from the interfering impurities, which is carried out by distilling it in the form of silicon tetrafluoride, silicohydrofluoric acid, or boron fluoride. Thus, for example, according to the method of Penfield [75, 76], the investigated sample is heated with sulfuric acid in the presence of silicon dioxide, and the formed silicon tetrafluoride

is absorbed by a solution of potassium fluoride in a 50% alcohol solution. The hydrochloric acid liberated during this process is titrated with an alkali. Armstrong [77] suggested an instrument for quantitative distillation of silicon tetrafluoride. The error of the method suggested by him for 0.1 g chemically pure sodium fluoride does not exceed 0.3 mg flourine, but for 0.1 g calcium fluoride to which 0.9 g calcium phosphate, 0.05 sodium nitrate, and 0.05 g sodium chloride have been preliminarily added, the magnitude of error fluctuated from 0.1 to 0.3 mg fluorine. Schrenk and Ode [78] distilled fluorine in the form of boron tetrafluoride or boron hydrofluoric acid after treating fluoride with boric acid in a mixture with perchloric or sulfuric acids. I. V. Tananayev [68] suggested a simpler method of separating fluorine, distilling it in the form of silicohydrofluoric acid. Raynes [67] made improvements in this method. /787

Willard and Winter [79] recommend adding a very small amount of zirconium-alizarin indicator and hydrochloric acid to the point of disappearance of color to the aqueous solution of the sample, in case of the presence of soluble fluorides alone in the analyzed substance and in the absence of interfering impurities. After adding an equal volume of ethyl alcohol, the obtained mixture is titrated with a standard solution of thorium nitrate until the appearance of a weak color. In the presence of impurities interfering with the determination, fluorine must be distilled in the form of silicon hydrofluoric acid. For this purpose, the analyzed substance is placed in a small distilling flask to which perchloric or sulfuric acid is added. Distillation is carried out at a temperature of 135°, which is maintained by periodically adding distilled water through a drip cock with a capillary tube. A small amount of zirconium-alizarin mixture and a solution of caustic soda is added to the distillate, collected in the amount of 50 - 70 ml, until the indicator color appears. Then an equal amount of ethyl alcohol is added, together with dilute acid, to the point of disappearance of the indicator color, after which the mixture is titrated with a mixture of thorium nitrate. This method was used to determine fluorine in fluorspar, apatite, phosphorite, cryolite, and other minerals and ores. The results obtained by Willard and Winter varied from the theoretical results by

0.002 - 0.2 mg fluorine per 50 mg sample. If the fluoride was not broken down by perchloric acid or contains a large amount of silica, preliminary fusion with soda is carried out. Distillation of fluorine in the form of silicon tetrafluoride or boron hydrofluoric acid is not recommended by the authors.

Boruff and Abbot [80] improved the Willard method. The control investigations of solutions containing from 0.5 to 5 mg/l sodium fluoride, 170 mg/l calcium bicarbonate, 150 mg/l magnesium sulfate, 30 mg/l sodium chloride, 100 mg/l ferric chloride, and 300 mg/l ammonium chloride yielded an error during analysis of $\pm$ 0.1 mg/l fluorine. These experiments also confirmed the opinion of Armstrong that during the titration of solutions containing less than 0.5 mg fluorine per liter, one should use a single alizarin-sodium sulfate salt as an indicator instead of the mixture of zirconium and alizarin red.

Winter and Budler [81] used the method of Willard and Winter to determine fluorine in plant materials that had been moistened with lime water before calcination. The authors indicate that the use of perchloric acid for distillation has the advantage over sulfuric acid that the latter can enter the distillate.

Hoskins and Ferris [82] used a 0.001 mol solution of thorium nitrate for the titration of fluorine; the indicator was a 0.05% solution of alizarin sodium sulfate. It is necessary to carefully regulate the pH of the solution, which must be 3.5. For this purpose, a buffer mixture consisting of monochloracetic acid and its salts was /788 used. The method of Hoskins and Ferris can be used to determine from 50 to 760 µg fluorine in 50 ml, and 6 to 90 µg in a mixture of 5 ml with an accuracy up to 1%.

Dahle and Wichman [83] established that the amount of fluorine determinable according to the method of Willard and Winter depends on the size of the distilling flask, the initial volume of solution, the amount of acid used, the initial concentration of fluorine in

the distilling flask, the temperature and rapidity of distillation, the volume of distillate, and the presence of impurities in the investigated material.

Dahle, Bonnar and Wichman [84] suggested the following method of determining small amounts of fluorine. Into one of two Nessler tubes having a capacity of 50 ml, 40 ml investigated solution is placed, while the same amount of distilled water is placed in the other tube, after which 1 ml 0.01% aqueous solution alizarin red is placed in both tubes. A 0.05 N solution of caustic soda is introduced into the investigated liquid until such time as the color is comparable with the pale rose color of the standard. Then, exactly 2 ml 0.05 N hydrochloric acid is added to each tube, and from a burette having a capacity of 10 ml and graduated to 0.05 ml, the investigated liquid is titrated with a solution of thorium nitrate containing 0.25 g $Th(NO_3)_4 \cdot 12H_2O$ per 1 liter, until such time as the color is a pale rose. Having noted the added volume of the thorium solution, exactly the same amount is added to the standard. To the latter liquid, now more intensely stained than the investigated liquid, a solution of sodium fluoride having a known concentration is added (0.01 mg/l fluorine) until an identical color is obtained in both tubes, after comparing the liquid volumes in them. Now the amount of fluorine in both tubes is identical. The rapidity of titration does not influence the results. Acidity has a quite strong value. The more suitable pH region is from 2.5 to 3.

P. K. Merwe [85] somewhat altered the method of Dahle, Bonnar, and Wichman, having employed preliminary distillation of fluorine in the form of silicon hydrofluoric acid. In one part of the distillate, the author determined acidity in the presence of alizarin red as an indicator, and in the other measured fluorine as a means of titration with thorium nitrate.

Clendon and Foster [86] developed a similar method of determining fluorine in food products containing 1 part fluorine by weight for 3 million parts substance, having used the thorium-alizarin lac for this purpose.

Hubbard and Henne [87, 88] developed a method of determining fluorine in gaseous organic substances. For this purpose, the investigated gas is broken down by passing it through a tube heated to 900° for combustion and filled with silica. The formed silicon tetrafluoride is captured using water or a mild alkali solution, and it titrated with cerium nitrate in the presence of methyl red or bromcreasol green. From 0.98 to 9.8 mg fluorine is determined with an accuracy of 2% using this method in 25 ml solution.

Scott and Henne [89] suggested a standard method of determining fluorine in plant and animal tissues. According to this method, the material is preliminarily treated with lime water of CaO, and heated at 600 - 700° for a period of 24 - 48 hours. From the dry residue, the fluorine is distilled in the form of silicon hydrofluoric acid and titrated with cerium nitrate or thorium in the presence of methyl red and bromcreasol green as indicators. According to the data of the authors, the detectable minimum is 20 μg fluorine. In samples weighing between 1 and 1.5 g, one can detect 0.02 to 5.0 mg fluorine.

Fairchild [90] changed the method of Greef as follows: for determining the excess of iron chloride, potassium iodide was added. The iodine separated out was titrated by thiosulfate. Verification of this method by other authors established that it gives results /789 which are too high [52, 91]. Proposed changes did not eliminate this disadvantage.

Kopfenberger [92] describes the following method of determining fluorine in the form of lead fluorochloride: to an investigated solution containing from 10 to 130 mg fluorine, 10 drops of methyl orange are added, the mixture is diluted up to 200 ml, and neutralized with caustic soda or hydrochloric acid. Then an excess of 0.5 ml 1 N hydrochloric acid is added. The mixture is heated to 55 degrees, and 250 ml solution $PbCl_2$ saturated at 55 degrees is added, slightly alkalized, and left for 12 hours. After filtering the precipitate that has fallen out and washing it with a saturated solution PbFCl and then water, the filter with the precipitate is put back in the

flask, 100 ml 0.75 N nitric acid is added, and it is heated for 5 minutes in a steam bath. The obtained solution is titrated with silver nitrate.

In 1939, the National Agricultural Chemical Association of the U.S.A. accepted a method based on the precipitation of fluorine in the form of PbFCl as a standard for determining fluorine in insecticides. Donovan (93) developed a detailed method of determining 10 - 100 mg fluorine using this method in poorly and easily soluble fluorides, as well as in the silicofluorides, both in the presence and absence of organic substances.

Mart'yanova [94] developed a method of determining fluorine in the presence of large amounts of chormates that precipitate in the form of silver chromate. The excess silver nitrate is precipitated by an alkali, and fluorine is determined in the filtrate by means of converting it to lead fluorochlorate with subsequent titration of the chlorine ions. This method can be used to determine 10 - 50 mg fluorine in 10 ml liquid containing 3 g CrO_3. The iron, silicic acid, and small amounts of sulfuric acid do not interfere with determination of fluorine.

Electrometric Methods

Treadwell [50, 96] suggested potentiometric titration of fluorine using the ferro-ferri electrode as an indicator. The method makes it possible to determine from 0.5 to 5 mg fluorine in 100 ml solution with an accuracy of up to 0.1 mg. The micro-apparatus used for this purpose can measure 0.05 mg fluorine. In the opinion of Harms and Iander [97], the potentiometric method makes it possible to measure 1 mg fluorine with an accuracy of up to 5%.

Allen and Furman [98] measured fluorine by potentiometric titration. For this purpose, $K_3[Fe(CN)_6]$ and a suspension of $KCe[Fe(CN)_6]$ are added to the fluoride solution. Then an amount of alcohol is added so as to obtain a 50% (by volume) alcohol solution.

The mixture, heated to 70 degrees, is titrated with a solution of cerium nitrate. This method produces good results with a content ranging from 0.1 to 50 mg fluorine, and with a small quantity of impurities.

Harms and Iander [97] recommend measuring small amounts of fluorine by a conductometric method based on the following reaction:

$$6NaF + AlCl_3 \rightleftarrows Na_3AlF_6 + 3NaCl.$$

Measurement is carried out in a buffer solution containing from 0.1 to 0.01 N acetic acid, twice that amount of sodium acetate, and 30% alcohol. Titration is carried out with a solution of aluminum chloride, using a microburette. This method can detect from 12 μg to 20 mg fluorine.

Flatt [99] developed potentiometric determination of fluorine based upon the property of salts of tetravalent uranium to yield poorly soluble binary salts of the M_1UF_5 type in combination with the alkali flourides. The method suggested by him consists in the following: the alkali solution of fluoride is titrated with a 0.05 mol solution of uranium sulfate using a platinum electrode. As the result of precipitation of the potassium uranofluoride, the comparatively high initial oxidative potential of the solution sharply drops at the equivalent point. In this case, the pH of the solution should be maintained at about 3.6, which is achieved by adding sulfanyl acid /790 to the titrated liquid; the sulfanyl acid is saturated with potassium sulfanylate. The accuracy of the method is about 1 μg fluorine. Using this method, one can measure up to 20 mg fluorine per liter.

Low [100] potentiometrically measured fluorine in natural waters by using the ferro-ferri electrode as an indicator. PO_4^{-3}, $C_2O_4^{-2}$, Al^{+3}, and Th^{+4} interfere with measurement. In the presence of impurities, fluorine is distilled. This method can measure from 0.2 to 60 mg fluorine per liter.

L. Langer [101] investigated the possibility of measuring small amounts of fluorine in solutions used to fix the terminal point of titration of the mercury drop electrode. He checked the reactions of fluorine precipitation in the form of calcium fluoride, lead fluoride, lanthanium fluoride, and thorium fluoride, as well as the reaction of the formation of complex ions $[FeF_6]^{-3}$, $[AlF_6]^{-3}$, and $[ZrF_6]^{-2}$. It was established that only titration with thorium and lanthanium salts yields satisfactory results. By employing a 0.01 N solution of thorium nitrate, one can titrate with an accuracy of up to 1% 0.2 mg fluorine in 50 ml 0.1-mol. solution potassium chloride or potassium nitrate.

In smaller volumes, one can titrate 0.005 mg fluorine with a 0.001 N solution of thorium nitrate.

Nichlos and Olsen [102] measured fluorine in organic compounds by preliminarily decomposing the sample in a nickel microcylinder with sodium peroxide and by titrating the obtained solution with a 0.01 N solution of cerium nitrate. The terminal point was determined either potentiometrically or by means of the conventional indicator method with the aid of methyl red. Potentiometric titration produced the best results. Sulfates interfere with this measurement.

Gravimetric Methods

Many authors consider that microbalance determination of fluorine in the form of calcium, thorium, lead, or lanthanium fluorides does not yield accurate results. In this case, one takes into account that the content in the investigated sample of less than 10 mg fluorine yields low results, while an amount of fluorine less than 1 mg cannot be determined by the microbalance at all.

Allen and Furman*, using the indications of Krausen and Becker [103], developed a method of determining small amounts of fluorine

*N. Allen and N. Furman. Journal of the American Chemical Society, Vol. 54, 1932, p. 25.

in the form of triphenyl stannous fluoride. The method they suggest consists in the following: at a pH of 7 - 9, a 2% alcohol solution of triphenyl stannous fluoride is added to the fluoride solution. After setting overnight, the precipitate that has fallen out is filtered and washed with alcohol and dried. According to the data of the authors, the results of measurements carried out by them using this method are very accurate. The highest accuracy lies in the limit of fluorine content ranging from 0.05 mg to 0.04 g. Moderate amounts of nitrates, chlorides, bromides, iodides, and sulfates do not interfere with measurement. Carbonates must be removed before precipitation, breaking them down with acid in the presence of phenophthalein. Silicic salts and phosphates must be preliminarily removed according to the method of Bercelius.

Miller [104] suggested a method of measuring fluorine in the form of a complex compound of benzidine and mercuric fluoride. Using this method, one can detect up to 40 μg fluorine in a 10 ml solution. The reagent is a solution of 1.84 g benzidine and 500 ml 0.02 N solution mercuric succinimide. For measurement, to the investigated liquid neutralized with caustic soda and once again mildly acidified with acetic acid, an excess amount of the referenced reagent is added at 50°, and kept for 20 minutes in a water bath; the /791
filtered precipitate is washed with cold water. The precipitate, dried over sulfuric acid or in a vacuum at 50°, has the composition $HgF_2(HF \cdot NH_2C_6H_4C_6H_4NH_2HF)_2$.

Nephelometric Methods

Stevens [105] developed a nephelometric method of determining the fluorine ion that consists in its precipitation in an alcohol solution in the form of calcium fluoride that falls out in a state of a very fine suspension which is quite stable in the presence of a protective colloid gelatin. According to the method of Stevens, one can determine from 1 to 2.5 mg fluorine in 25 ml solution. The measurement is interfered with by arsenate, chromate, sulfate, silicate and phosphorate salts, as well as the salts of aluminum, which

should be preliminarily removed according to a method described by the author. The error of measurement is up to 1%.

Gas Volume Determination of Elementary Fluorine

Gas volume determination of elementary fluorine, described for macroamounts by Miller [106], is hardly applicable for determining small amounts of fluorine.

Glass Etching Method

The test for glass etching, usually employed for qualitative determination of fluorine, can also be used for an approximate estimate of the quantitative content of this element.

Carlos [107] used this method during his analysis of mineral water for the presence of fluorine, considering it possible to determine 40 - 50 mg fluorine per liter.

Olivier [8] developed a method of approximate quantitative determination of fluorine based on a comparison of glass sheets following etching. In this case, depending upon the fluorine content, treatment of the glass should be carried out variously. For example, according to the so-called "crucible" method, which is an approximate one, up to 0.02% fluorine can be determined. Then the "beaker" method makes it possible to determine up to 0.05 mg fluorine according to the etched fissure. Finally, by the aid of the method of "spot fissures", up to 0.1 µg fluorine can be determined.

Spielhaczeck [108] determined fluorine in sulfuric acid and oleum according to glass etching within limits of 0.1 to 100 mg fluorine by comparing it with a scale of standards. The detectable minimum is 10 µg.

Spectroscopic Methods

Petrey [109] determined fluorine spectroscopically in drinking water. The best results were achieved with a fluorine content ranging from 0.05 to 1.5%.

Karreth [110] developed an apparatus in which the formation of silicon tetrafluoride occurs with its absorption by an alloy consisting of 10 parts PbO and 90 parts B_2O_3 for subsequent spectral determination of fluorine. The mean error comprised 1.5%.

Datta [111] obtained alkali earth fluoride for analysis, and studied their spectra. The apparatus he employed is an automatic quartz spectrograph. The results of analyzing phosphorites containing 0.02% fluorine correspond with the results of chemical analysis.

Comparative Characteristics of Different Methods of Determining Fluorine

Smit [91] first used a comparison of methods of determining fluorine suggested before his time by Fairchild [90], Foster [52], Willard and Winter [79], and Sanchis [53]. The results of comparison showed that the Fairchild method always yields excessively high results, while the other three methods generally produce identical results of analysis.

Dahle [112] compared methods suggested by Foster, Willard and Winter, and Steiger. The investigated solution contained 2.08 mg fluorine per liter. During the analysis, it was found that the method of Foster found 2.08 mg fluorine, while the method of Willard and Winter detected 2.2 mg, and that of Steiger found 1.9 mg fluorine per liter. /792

Associates of the Laboratory of the Leningrad City Department of Public Health [113] carried out a detailed check under various experimental conditions of the sensitivity and accuracy of the

methods of quantitatively determining fluorine in water as suggested by Sanchis, Foster, Willard and Winter, Boruff and Abbot, and the authors.

The combined methods suggested by the authors proved to be the simplest, most sensitive, and most accurate for determining fluorine in drinking water, particularly that containing hundredths of a part of 1 mg fluorine per liter.

Hackl [114] measured 0.3 mg fluorine in 1 g sample using the titanium method. He indicates that the Foster method is most sensitive.

The data cited in Table 2 show that one can detect from 0.5 to 500 mg fluorine according to the coloration of complex compounds of titanium, but according to the color of complex compounds of iron one can determine from 0.25 to 50 mg fluorine per liter of solution. The zirconium compounds used for the analysis make it possible to determine from 0.04 mg to 7.5 g per liter of solution. The volumetric methods can determine from 0.5 mg, while the electrochemical methods determine from 0.2 mg to 2 g per liter. In most cases, the phosphates, borates, and a number of other ions interfere with the measurement of fluorine.

In order to obtain accurate results in the presence of impurities that interfere with analysis, it is vital to preliminarily distill the fluorine in the form of silicon hydrofluoric acid.

TABLE 2. A COMPARATIVE TABLE OF DIFFERENT METHODS OF QUANTITATIVELY DETERMINING FLUORINE

Author	Determinable amount, length of analysis	Author	Determinable amount, length of analysis
Colorimetric method			
a) Titanium compounds		c) Zirconium, thorium and cerium compounds	
Steiger [27]	From 0.75 mg per 1.5 ml	De-Boer	120 - 150 mg
Mervin [44]	From 0.5 to 4 mg per 100 ml	Thompson [60]	0.8 - 1.6 mg/l, 4 hours. Error: 0.05 mg/l
Gol'denberg [26]	From 0.1 to 1 mg per 25 ml	Elvove [61]	0.8 - 1 mg/l, 18 hrs. Error: 1.5%
Korenman [35]	From 0.04 to 0.5 mg HF in 25 ml Error: 1 - 2.5%	Bar [62]	5 mg/l. Error: 0.1 mg/l
Hackl [115]	From 0.2 to 0.5 mg in 1 ml	Sanchis [53, 54]	Up to 3 mg/l, 4 hrs. Error: 0.1 mg/l
Shvedov [48]	From 0.55 to 5 mg/l, 1 hour Error: 0.1 - 0.2 mg/l	Biogeochemical Lab. of the Academy of Sciences, USSR [63]	From 0.1 to 2.5 mg/l. Error: 0.01 mg/l
b) Iron compounds		Laboratory of Communal Hygiene [65]	0.04 - 0.08 mg/l, 12 - 16 hrs.
Greef [23]	From 0.2 g in 25 ml	Shvedov [48]	2 mg/l, 18 hours. Error: 1.5%
Smit [22]	From 0.05 to 0.5 mg in 10 ml	Raynes [67]	From 2.01 to 2.0 mg in 100 ml
Foster [51, 52]	From 0.025 to 0.25 mg in 75 ml	Raynes [69]	0.001 - 0.003 mg in 25 ml, 10 min
Chemodanova [25]	0.025 to 0.35 mg/l in 25 ml solution 0.001 - 0.015 mg/l HF in 1 l air	Larmar [70]	Up to 0.12 mg in 100 ml, 18 hrs
Shakhkel'din [55]	Up to 3 mg in 100 ml, error: 1.3%	Smit [95]	Up to 0.1 mg in 50 ml
Fel'dman [56]	0.004 - 0.032 mg/l air	Kolthoff [37]	From 0.01 to 15 mg in 2 ml. Error: 3 - 4%
Armstrong [57]	From 0.25 to 0.5 mg in 25 ml. Error: 0.1 mg/l	Talvitie [71]	1 mg/l

(Table continued on following page)

TABLE 2. (continued)

Author	Determinable amount, length of analysis
Colorimetric method	
c) Zirconium, thorium, and cerium compounds (cont.)	
Hammond [118]	From 2 to 50 μg fluorine in 10 ml. Error: 1 - 3%
d) Various colorimetric methods	
Osherovich [72]	0.06 - 0.14 mg in 100 ml, 4 hrs. Error: 5 - 6%
Shvedov [73]	0.01 mg/l, 2 - 5 hours
Faney [74]	2 mg/l
Volumetric methods	
Willard [79]	From 0.152 to 15 mg in 40 ml. Error 0.002 - 0.2 mg
Boruff [80]	From 0.5 to 5 mg/l Error: 0.1 mg/l
Hoskins [82]	From 57 to 760 μg in 50 ml. From 6 to 90 μg in 5 ml. Error: 1%
Armstrong [116]	From 2 to 25 g in 1 ml. Error: 2%
McGlure [117]	50 - 100 μg in 0.5 g. Error 5 μg in 0.5 g substance
Merwe [85]	0.1 mg in 40 ml
Clendon [86]	1 part fluoride for 3 million parts substance
Hubbard [87, 88]	0.98-9.8 mg fluorine in 25 ml. Error: 2%
Scott [89]	From 0.02 to 5.0 mg flourine in 1 - 1.5 g. Error: 0.3 - 6%
Kopfenberger (92)	10 - 130 mg fluorine in 0.5 l, 12 - 14 hrs
Mart'yanova [94]	10 - 50 mg in 10 ml
Electrometric methods	
Treadwell [50, 96]	From 0.5 to 5 mg fluorine in 100 ml. Error: 0.1 mg
Allen [98]	From 0.1 mg in 2 ml to 50 mg in 25 ml. Error ranges from 0.5% - 5%
Harms [97]	10 μg in 1 ml and 250 μg in 3 ml. Error up to 5%
Low [100]	0.2 - 60 mg/l. Error: 1%
Langer [101]	From 5 to 200 μg in 50 ml. Error: 1%
Nichlos [102]	From 1 to 10 mg in 10 ml
Gravimetric method	
Allen [98]	From 0.05 to 40 mg, 12 hours

(Table concluded on following page)

TABLE 2. (concluded)

Author	Determinable amount, length of analysis	Author	Determinable amount, length of analysis
Nepholometric method		Studies of 1945 - 1946 (continued)	
Stevens [105]	1 - 2.5 mg in 25 ml. Error: 1%	Crossley [125]	From 10 to 180 μg in 100 ml
Studies of 1945 - 1946		Matuszak [126]	From 0.0005 to 0.1% organic fluorides in hydrocarbons. Error: 0.2 - 1%
Williams [120]	From 0.5 to 150 μg in 50 ml. Error up to 2%	Clifford [127]	From 0.02 to 236 parts fluorine in 1 million parts substance
Ovenston [121]	From 0.1 to 1% inorganic fluorides in 5 g organic substances. Error ranges from 0.5 to 2.5%	Godfrey [128]	10 mg fluorine in 10 ml. Error ranges from 1 to 5%
Lamar [122]	From 0.02 to 0.16 mg in 100 ml, 12 hours		
Cade [123]	From 0.005 to 0.3% H_2SiF_6 in HF. Error 0.003%		
Harvey [124]	From 3 to 9 parts fluorine per 1 million parts substance		

Note. In the determination of fluorine, the authors of a number of studies [63, 65, 66, 69, 37, 80, 116, 85, 86, 95] preliminarily distilled the fluorine.

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